HYSPLIT Simulations for ALOHA Chemicals: Possibilities and Suggestions

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Highly abbreviated and slightly edited version of Dec 4, 2018 Presentation for use in Aug 27, 2019 meeting

1. Physical-Chemical Properties
2. Simulation Testbed
3. Simulation Results
4. Products
5. Recommendations

1. **Physical-Chemical Properties**
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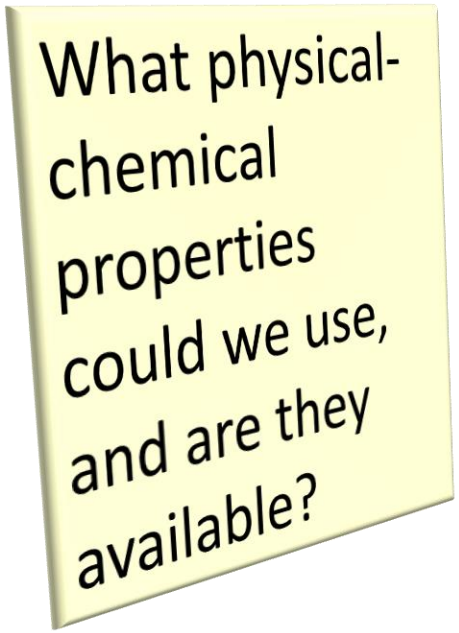
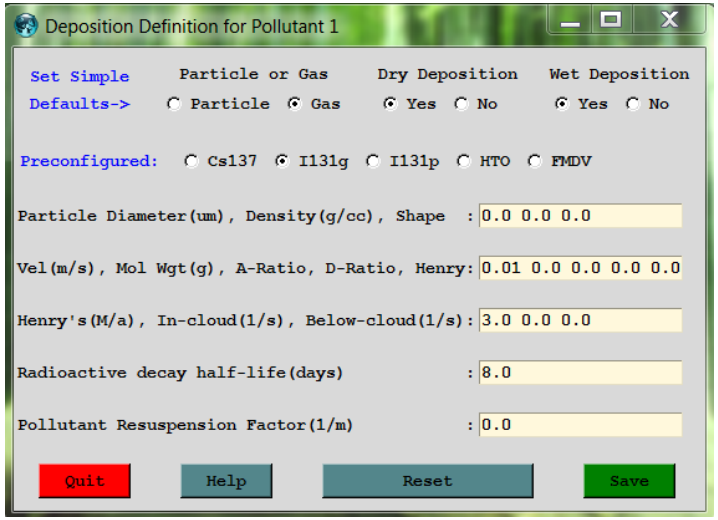


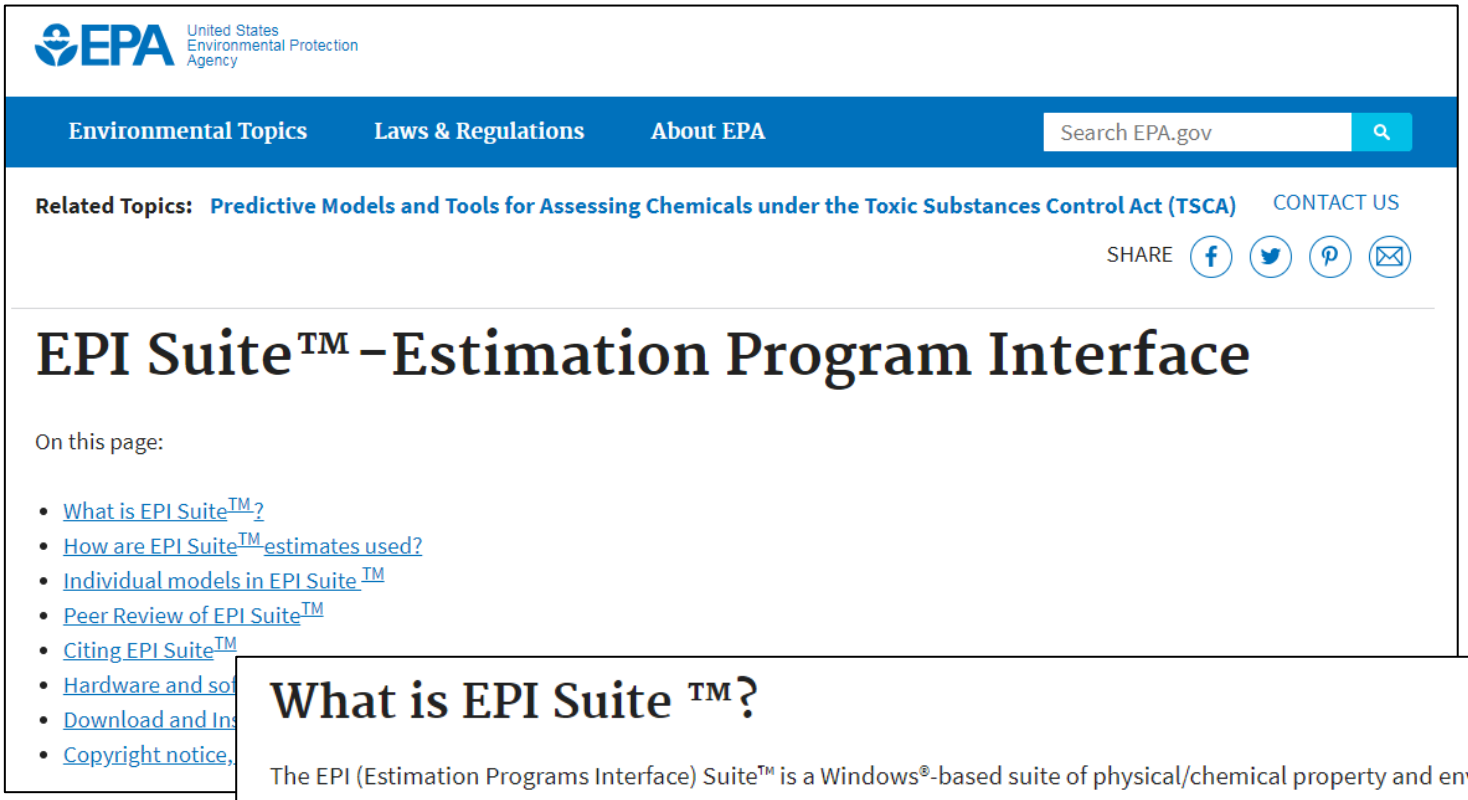
What physical-chemical properties could we conceivably use in HYSPLIT, if we had them?

- **Phase in the atmosphere** *(e.g., vapor vs. particle)*
- **Dry Deposition Parameters**
  - if particle: *particle size, density, shape factor*
  - if vapor: *surface reactivity factor, diffusivity ratio, effective Henry's Law Constant*
  - *or could specify fixed dry deposition velocity*



- **Wet Deposition Parameters**
  - if particle: *could probably use HYSPLIT defaults, as behavior more dependent on particles than actual chemical*
  - if vapor: *Henry's Law Constant*
- **Chemical Reactivity Parameters**
  - *e.g., half-life for reactions with OH•, O_3, etc…*
  - *Can use as "radioactive decay half-life", or implemented with chemrate.txt*
  - *but how to provide reactant concentrations, e.g., conc. of OH•, O_3, etc.?*

First: used EPA's Estimation Program Suite



https://www.epa.gov/tsca-screening-tools/epi-suitetm-estimation-program-interface

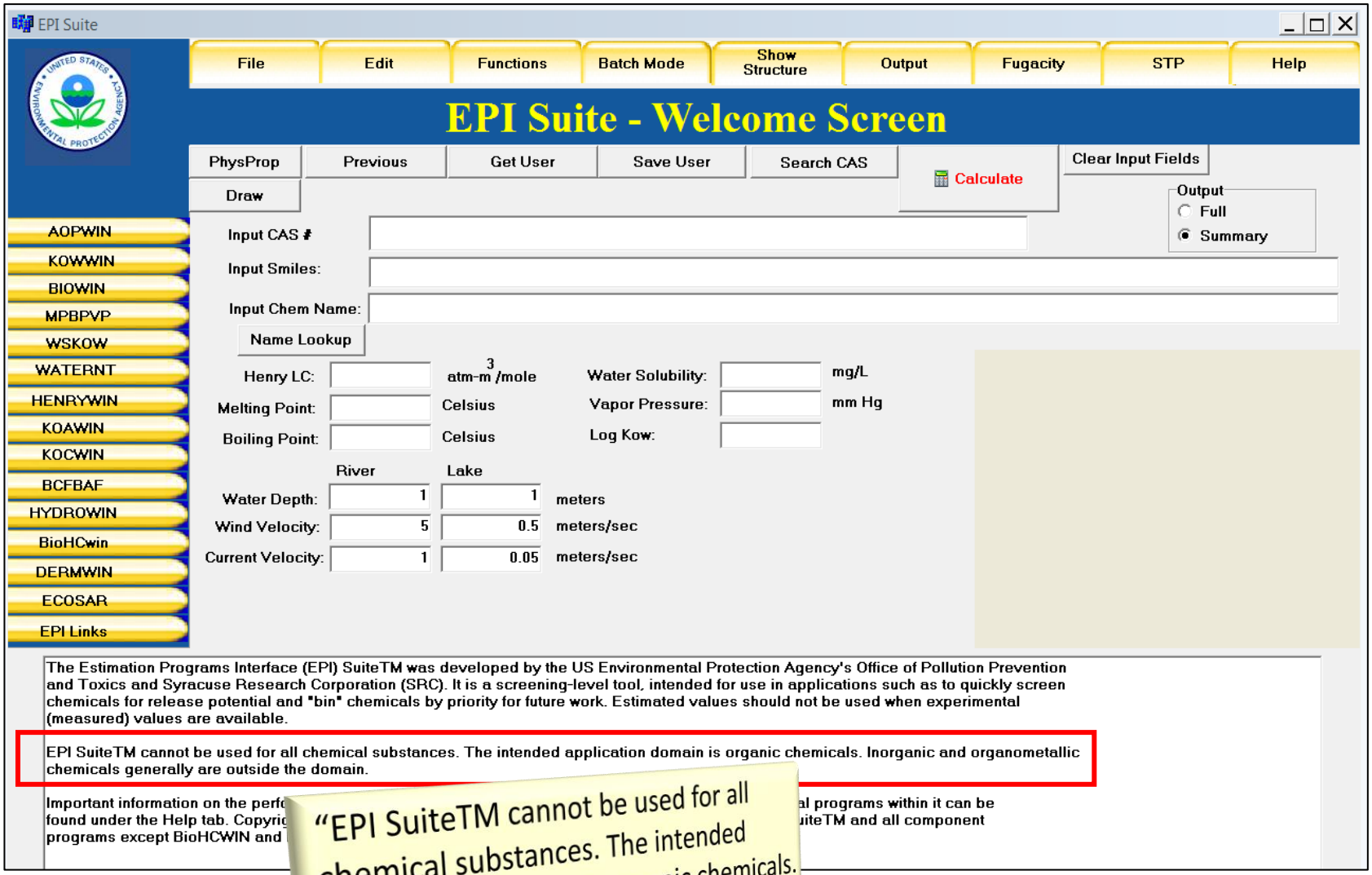
What is EPI Suite ™?

The EPI (Estimation Programs Interface) Suite™ is a Windows®-based suite of physical/chemical property and environmental fate estimation programs developed by EPA's and Syracuse Research Corp. (SRC).

EPI Suite™ uses a single input to run the following estimation programs: KOWWIN™, AOPWIN™, HENRYWIN™, MPBPWIN™, BIOWIN™, BioHCwin, KOCWIN™, WSKOWWIN™, WATERNT™, BCFBAF™, HYDROWIN™, KOAWIN and AEROWIN™, and the fate models WVOLWIN™, STPWIN™ and LEV3EPI™. ECOSAR™, which estimates ecotoxicity, is also included in EPI Suite™.

EPI Suite™ is a screening-level tool and should not be used if acceptable measured values are available.

A clear understanding of the estimation methods and their appropriate application is very important. Click on the Help tab in EPI Suite™ for detailed information on the methods and models in it.



"EPI SuiteTM cannot be used for all chemical substances. The intended application domain is organic chemicals. Inorganic and organometallic chemicals generally are outside the domain."

(but, for many of the non-organic ALOHA chemicals, experimental values are provided…..)

Created a large spreadsheet with all physical-chemical properties and related information collected, with one row for each of the 811 ALOHA substances being considered here

			IY	IZ	JA	JB	JC	JD	JE	JF	JG
				778	759	473	486	776	779	779	9
				HenryWin	HenryWin	HenryWin	HenryWin	HenryWin			770
				22-Jun-18	22-Jun-18	22-Jun-18	22-Jun-18	22-Jun-18			32
					Henry's Law Coeff	Henry's Law Coeff	Henry's Law Coeff		Henry's Law Coeff	Henry's Law Coeff	
					Bond Estimated	Group Estimated	Experimental		synthesized	synthesized	
CAS Number without leading zeroes	SMILES	Name		CAS	atm-m3/mole	atm-m3/mole	atm-m3/mole	SMILES	atm-m3/mole	molar/atm	basis
999-55-3	O=C(OCC=C)C=C	**2-Propenoic acid, 2-propenyl ester**		000999-55-3	1.21E-04	6.43E-05		O=C(OCC=C)C=C	**9.27E-05**	**1.08E+01**	using avg of bond- and group-estimated
4602-84-0	OCC=C(CCC=C(CCC=C(C)C)C)C	**2,6,10-Dodecatrien-1-ol, 3,7,11-trimethyl-**		004602-84-0	2.52E-04	1.73E-05		OCC=C(CCC=C(CCC=C(C)C)C)C	**1.35E-04**	**7.43E+00**	using avg of bond- and group-estimated
2050-92-2	N(CCCCC)CCCCC	**1-Pentanamine, N-pentyl-**		002050-92-2	1.60E-04	2.08E-04		N(CCCCC)CCCCC	**1.84E-04**	**5.43E+00**	using avg of bond- and group-estimated
927-62-8	N(CCCC)(C)C	**1-Butanamine, N,N-dimethyl-**		000927-62-8	8.54E-05	3.08E-04		N(CCCC)(C)C	**1.97E-04**	**5.08E+00**	using avg of bond- and group-estimated
622-45-7	O=C(OC(CCCC1)C1)C	**Acetic acid, cyclohexyl ester**		000622-45-7	3.19E-04	1.20E-04		O=C(OC(CCCC1)C1)C	**2.20E-04**	**4.56E+00**	using avg of bond- and group-estimated

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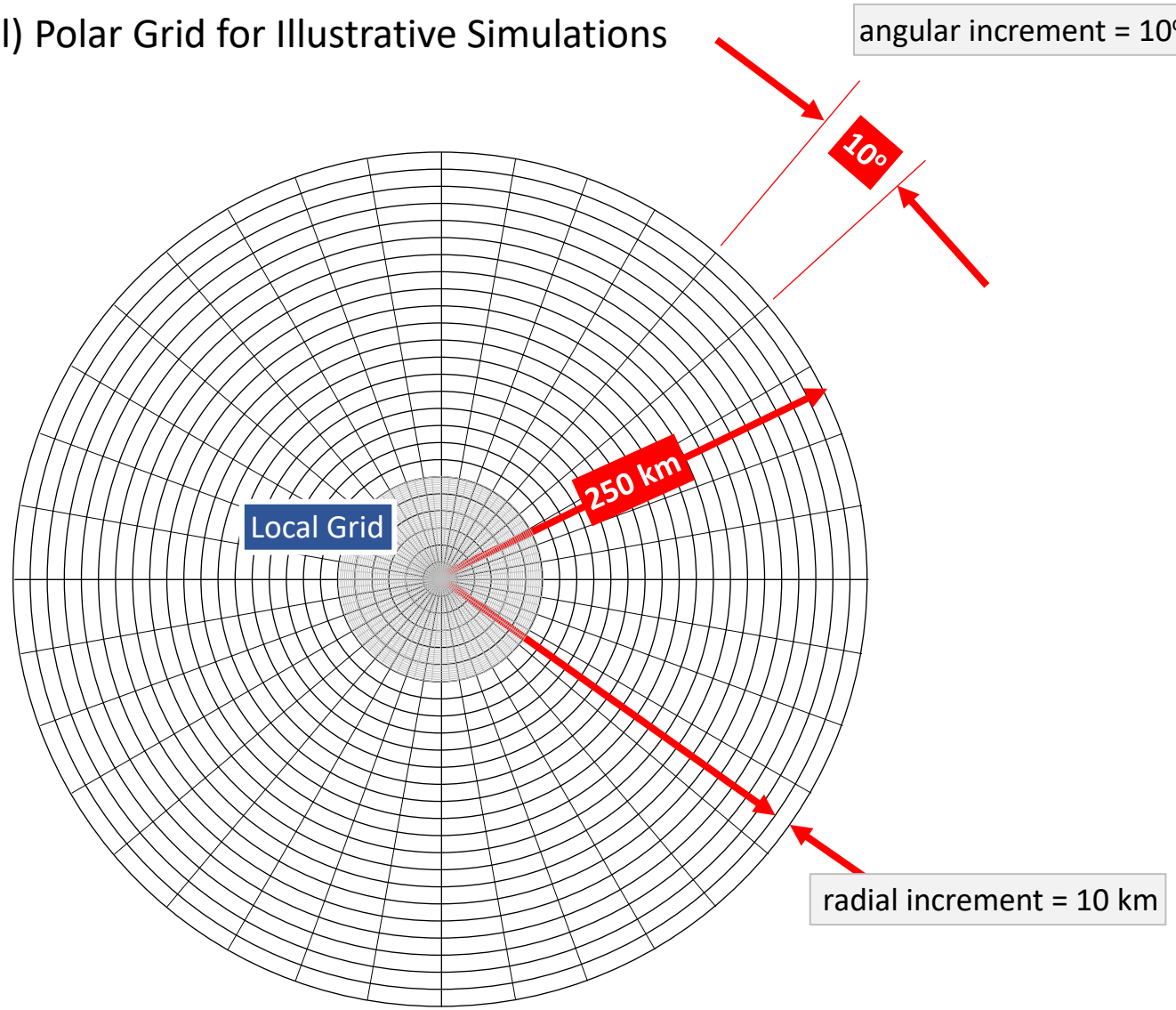
In order to get a sense of how the physical-chemical parameters affect the simulated downwind concentrations, created a "simulation test-bed"

Simulation Test-Bed

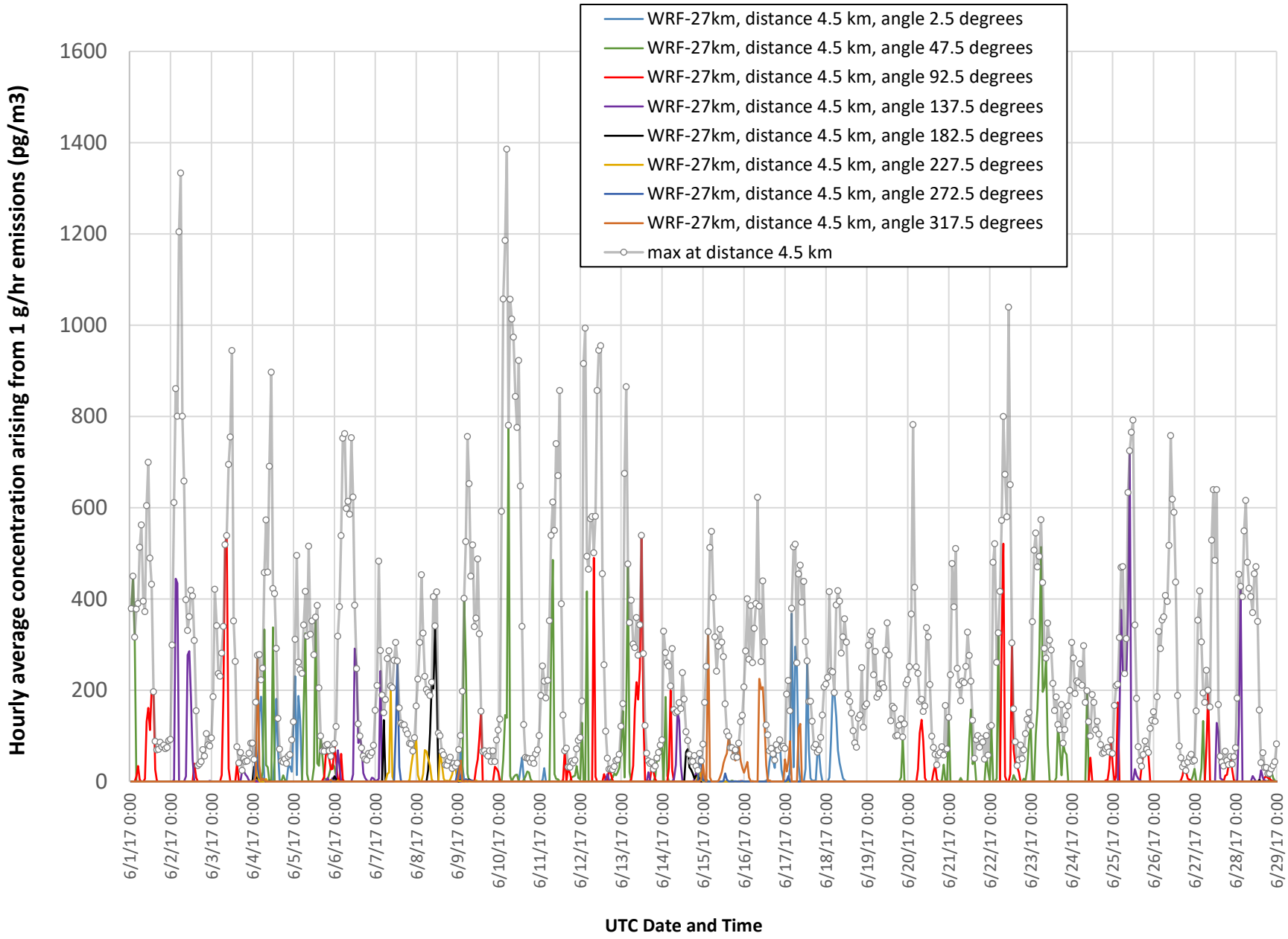
- Used NCWCP as source location (latitude = 38.9721, longitude = -76.9248)
- Used height of emission = 10 m
- Did not use any plume rise
- Always emitted 1 gram per hour
- Used a “local” (0-50 km) and “regional” (0-250 km) polar grid
- Concentration grid output averaging time = 1 hour (+ whole-run averages)
- Results shown for lowest concentration layer = 0-100 meters
- 4-week (672 hour) simulations, with a 4-day spin-up before sampling began
- Four months in 2017: March, June, September, and December
- WRF-27km and NAM-12km met data were used
- Varied simulation & dispersion parameters – to establish simulation testbed
- Then, varied physical-chemical properties to investigate effects of differences

Regional (and Local) Polar Grid for Illustrative Simulations

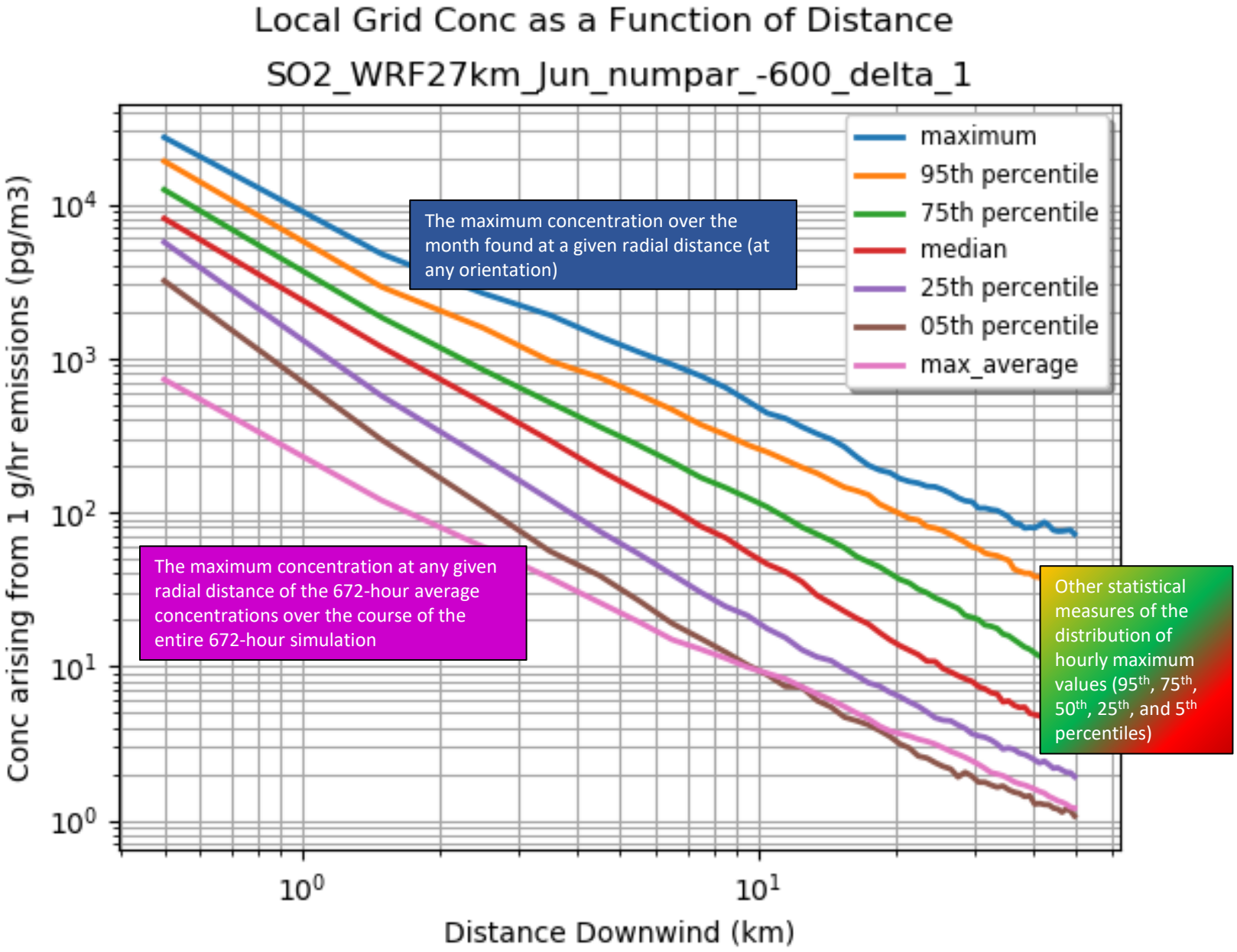


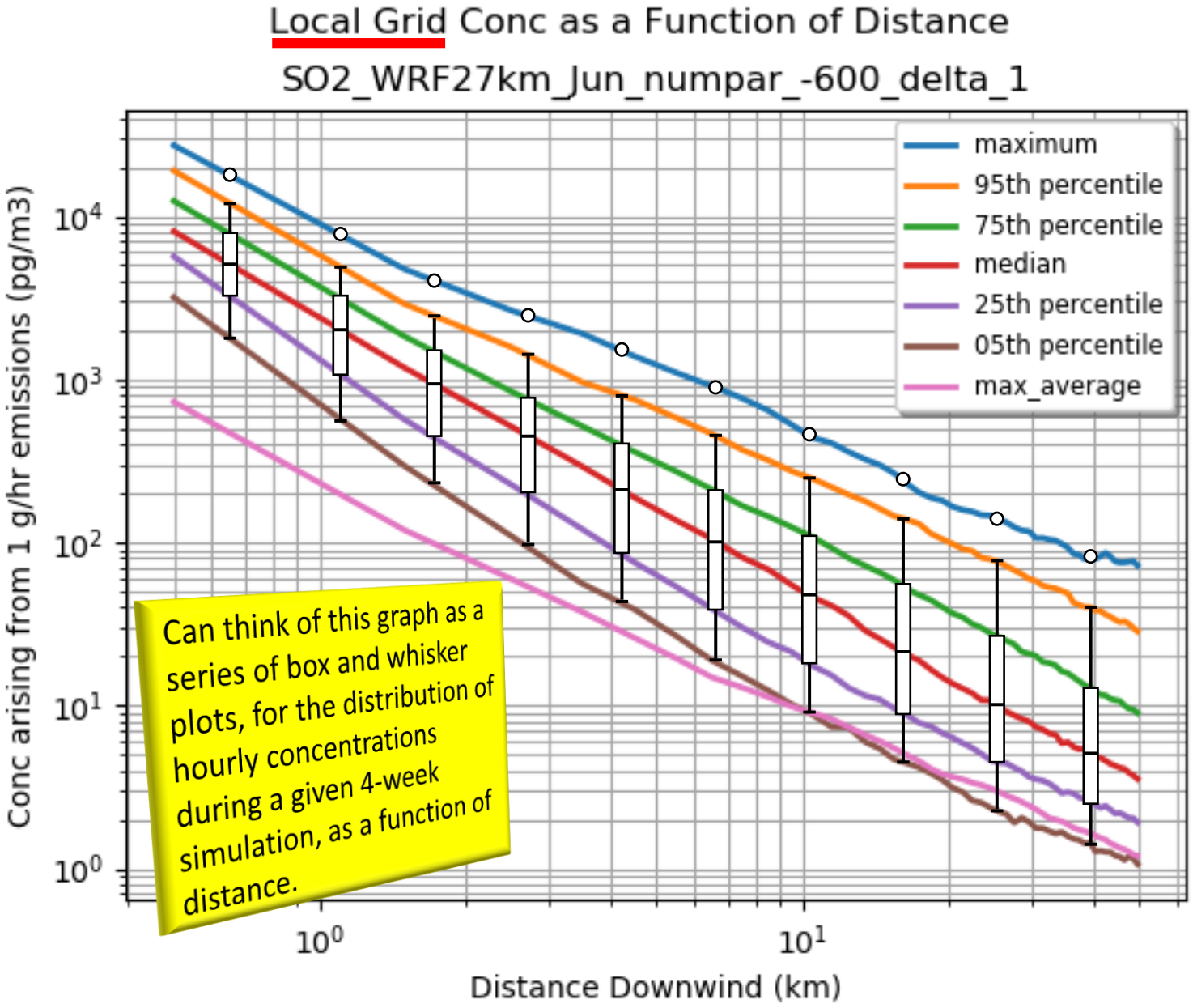
- Uncertainty using wind-field data of limited spatial resolution.
- Difficult to compare different simulations at any given location
- Focused on the maximum concentrations simulated as a function of distance away from the source, independent of angular orientation from the source.
- FORTRAN program to extract these max concentrations.
- “Includes” the effects of horizontal dispersion, e.g., as the maximum concentrations at any distance will be diminished the greater the horizontal dispersion is, etc.

Hourly concentrations at 4.5 km from the source at different angular orientations (WRF-27km met data).



A program was written to calculate the statistical distribution of the hourly maximum concentrations at each radial distance over the course of a given 4-week simulation




Local Grid Conc as a Function of Distance
SO2_WRF27km_Jun_numpar_-600_delta_1
maximum
95th percentile
75th percentile
median
25th percentile
05th percentile
max_average
Conc arising from 1 g/hr emissions (pg/m3)
10^4
10^3
10^2
10^1
10^0
10^0
10^1
Distance Downwind (km)
Can think of this graph as a series of box and whisker plots, for the distribution of hourly concentrations during a given 4-week simulation, as a function of distance.

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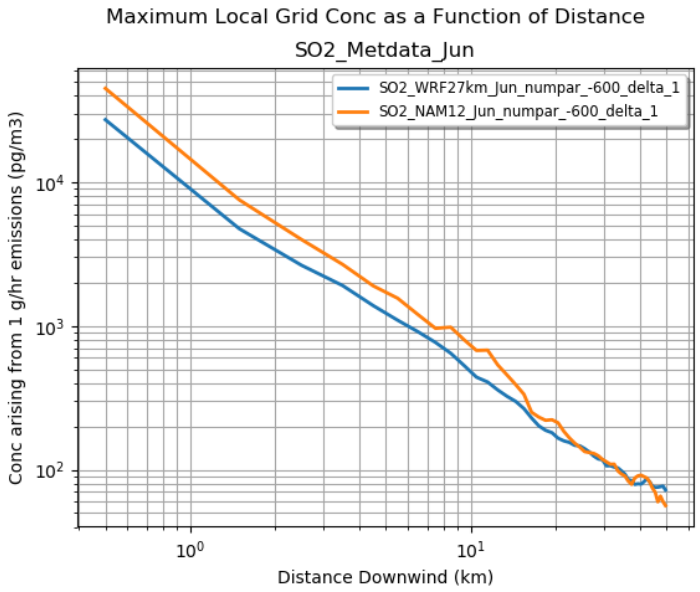
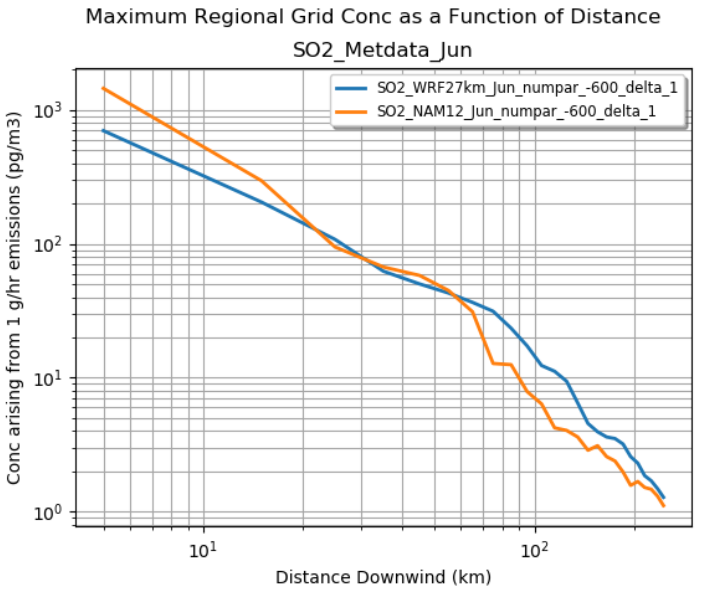
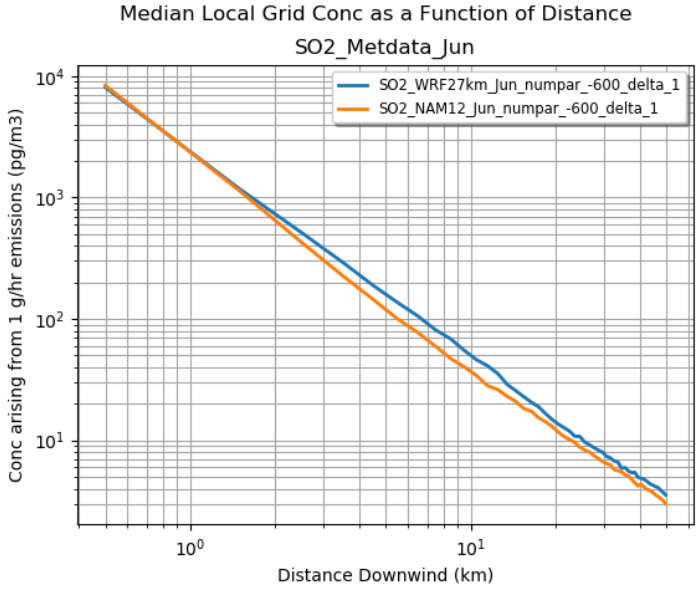
How much are results influenced by uncertainties in physical-chemical properties?

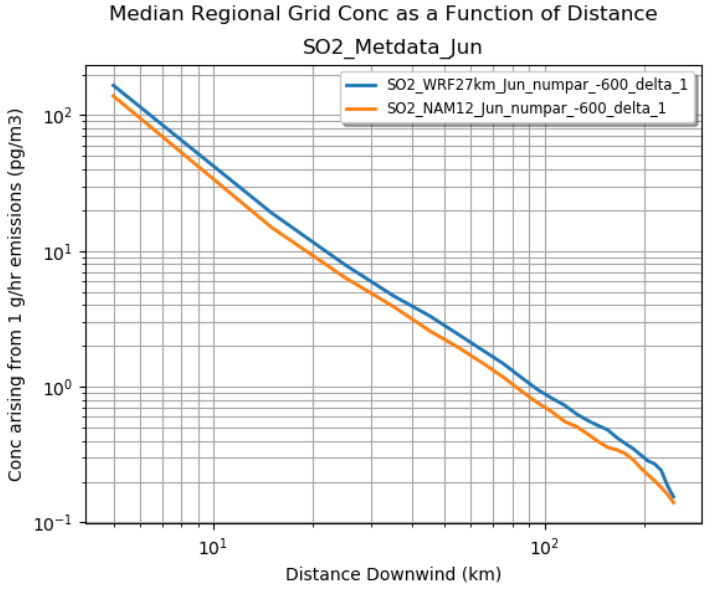




Differences in simulated concentrations if different met data is used...

Keep this in mind when considering differences arising from different pollutant parameter choices





What physical-chemical properties could we conceivably use in HYSPLIT, if we had them?

- **Predicted phase in the atmosphere** *(e.g., vapor vs. particle)*

- **Dry Deposition Parameters**
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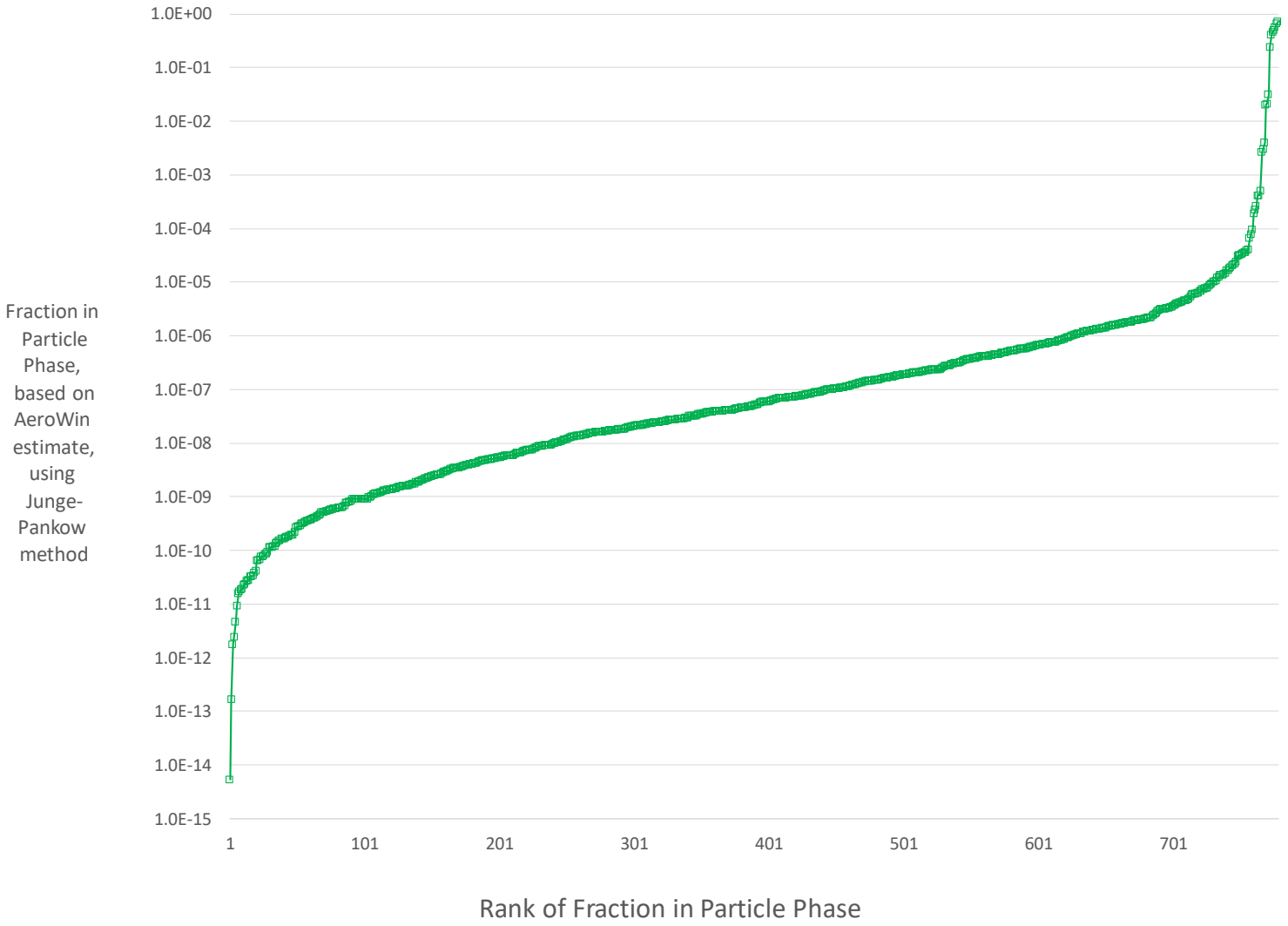
  - if vapor: *surface reactivity factor, diffusivity ratio, effective Henry's Law Constant*

- **Wet Deposition Parameters**
  - if particle: *could probably use HYSPLIT defaults*
  - if vapor: *Henry's Law Constant*

- **Chemical Reactivity Parameters**
  - *e.g., half-life for reactions with OH•, O_3, etc.*


Fraction in Particle Phase, based on AeroWin estimate, using Junge-Pankow method
1.0E+00
1.0E-01
1.0E-02
1.0E-03
1.0E-04
1.0E-05
1.0E-06
1.0E-07
1.0E-08
1.0E-09
1.0E-10
1.0E-11
1.0E-12
1.0E-13
1.0E-14
1.0E-15
1
101
201
301
401
501
601
701
Rank of Fraction in Particle Phase

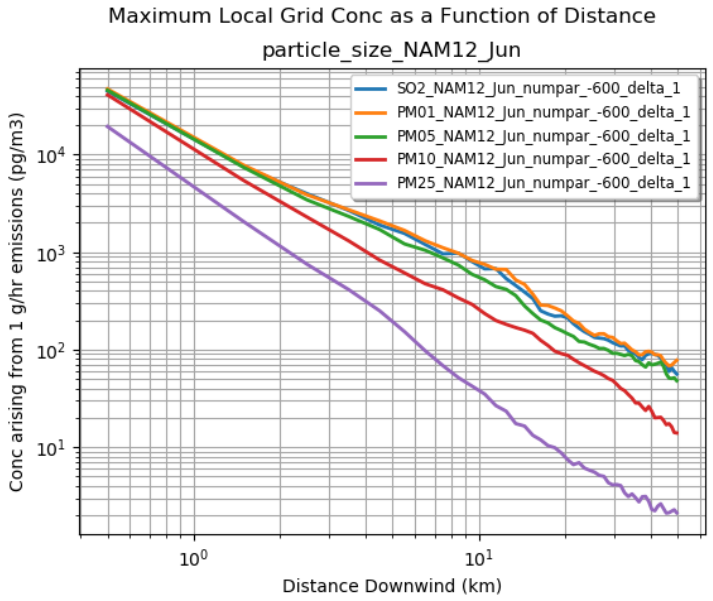
Most ALOHA chemicals would appear to be primarily in the vapor phase in the atmosphere, according to conventional empirically-driven vapor-particle partitioning correlations

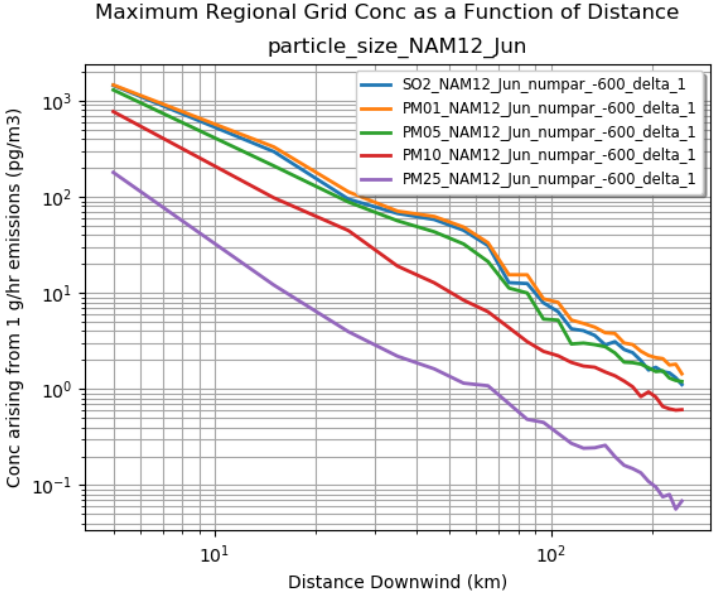
- but, the behavior can be complex, e.g., when droplets are present and the compound is relatively soluble in water; although in this case, one would have to know things like the effective Henry's Law Constant and the Liquid Water Content of the atmosphere, as well as impacts of mass-transfer limitations, to make any kind of estimate of absorption into droplets

- A few of the ALOHA chemicals are "solids" at typical temperatures and pressures, but this does not mean that the form of the compound emitted to the air will be a solid. In these cases, it is likely that the emitted form is a gas that may or may not subsequently become associated with atmospheric particulate

- Upshot – most likely, best to assume that chemicals in the vapor phase, unless some special information is available

- Example simulations demonstrate that it does not make a huge difference one way or another, especially for relatively short range fate and transport simulations.

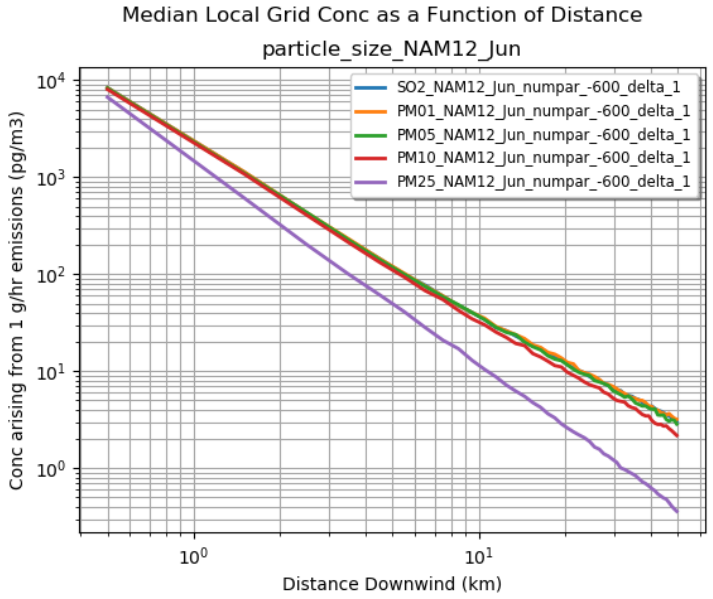


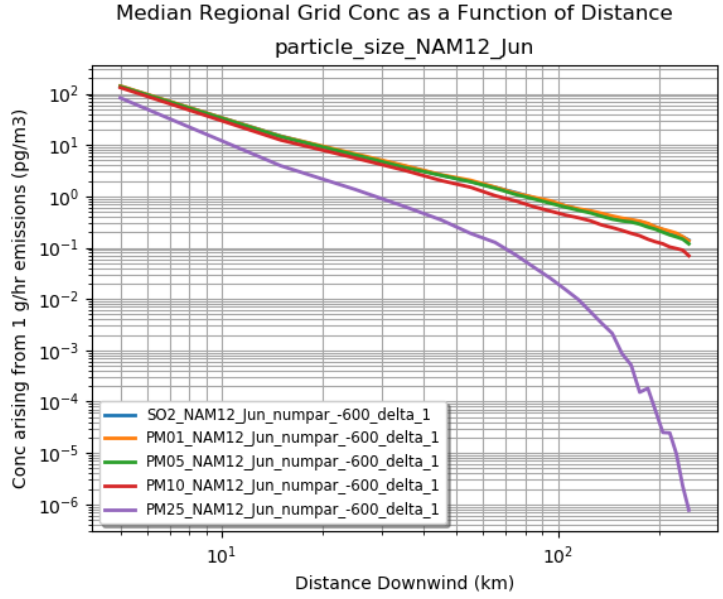


Not a very dramatic difference between gas-phase SO_2, and 1 and 5 µm particles

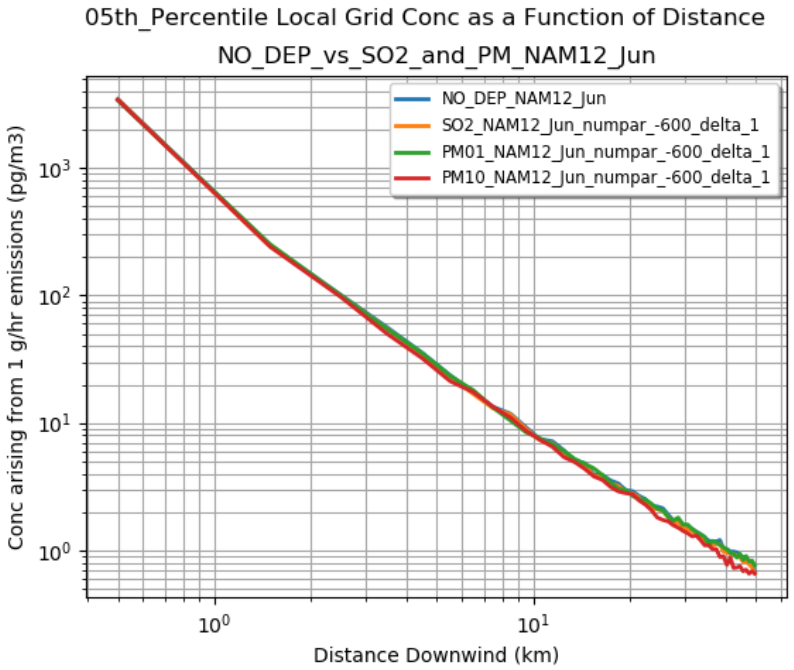
If pollutant partitions to atmospheric particles, most would be associated with particles less than 5 µm

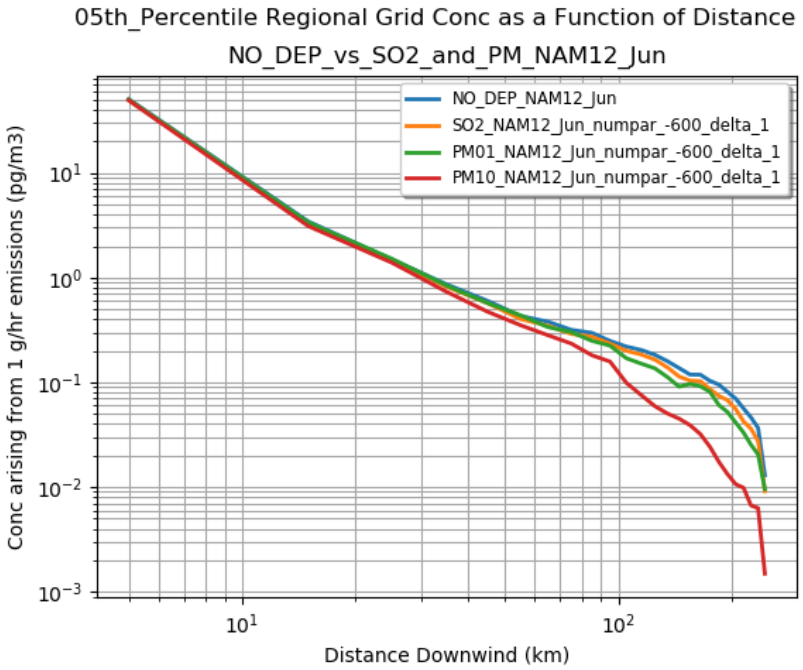
Bigger differences seen with 10 and 25 µm particles





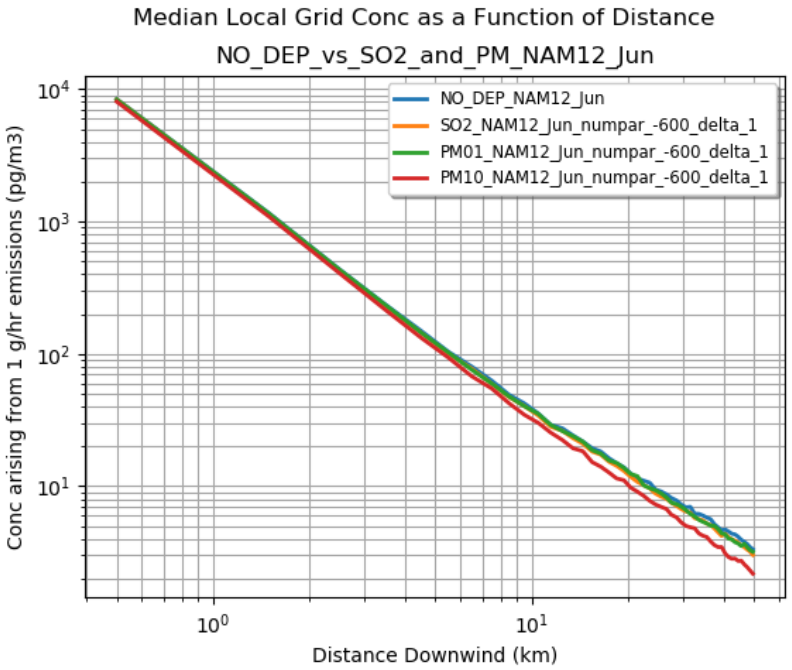
Compare simulation with no deposition with simulation of SO2, PM01 and PM10 with default deposition parameters

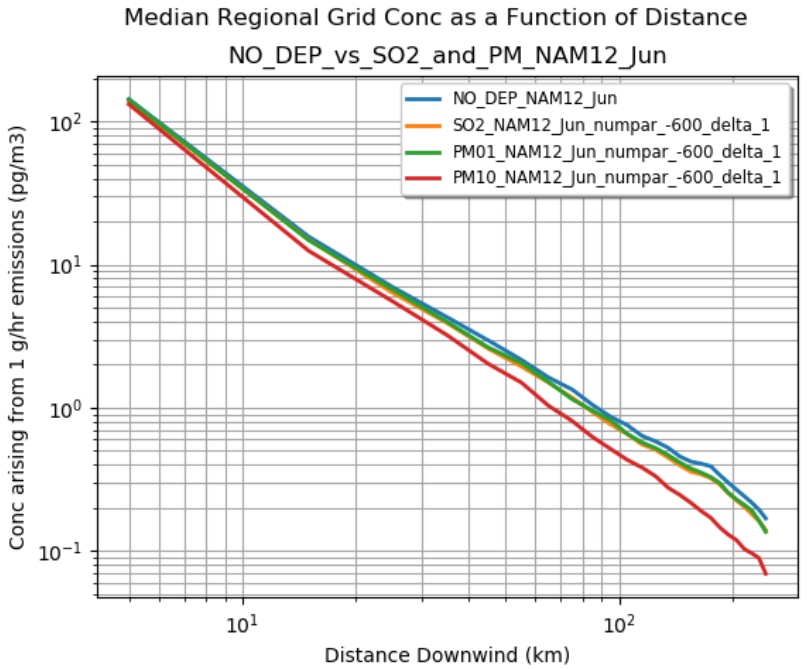




For 5th percentile, where one might expect to see the consequences of deposition (e.g., when it is raining), little difference except for large distances with large particles (10 µm)

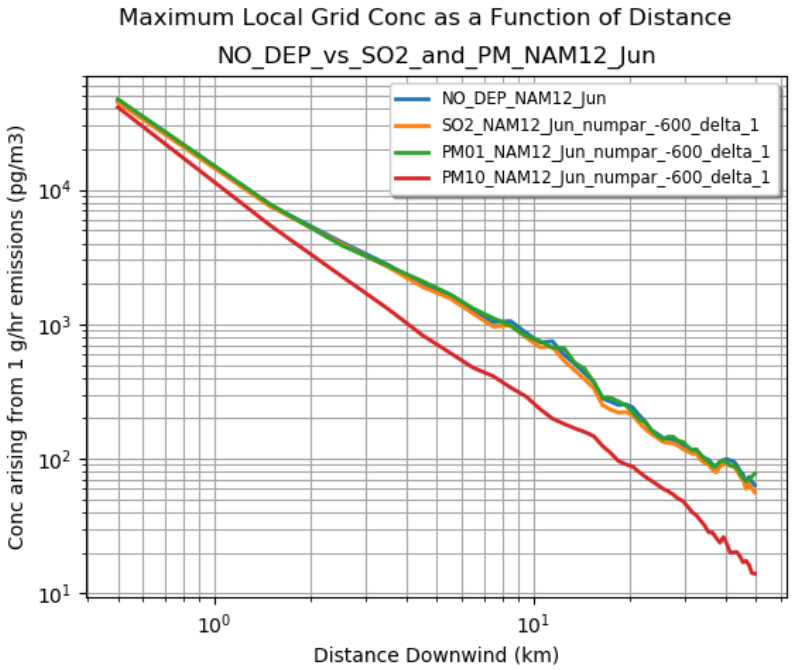
Compare simulation with no deposition with simulation of SO2, PM01 and PM10 with default deposition parameters

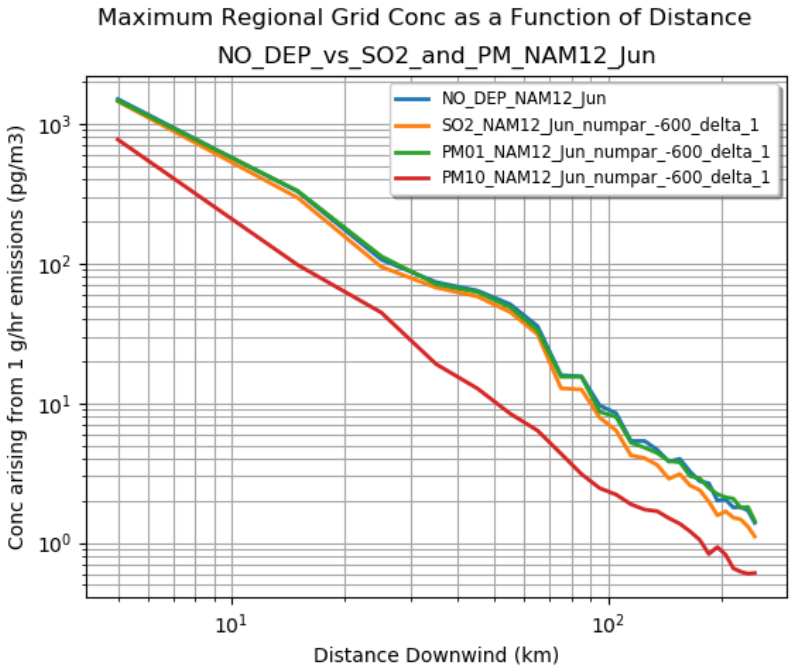




For median concentrations, little difference except for large particles (10 µm)

Compare simulation with no deposition with simulation of SO2, PM01 and PM10 with default deposition parameters





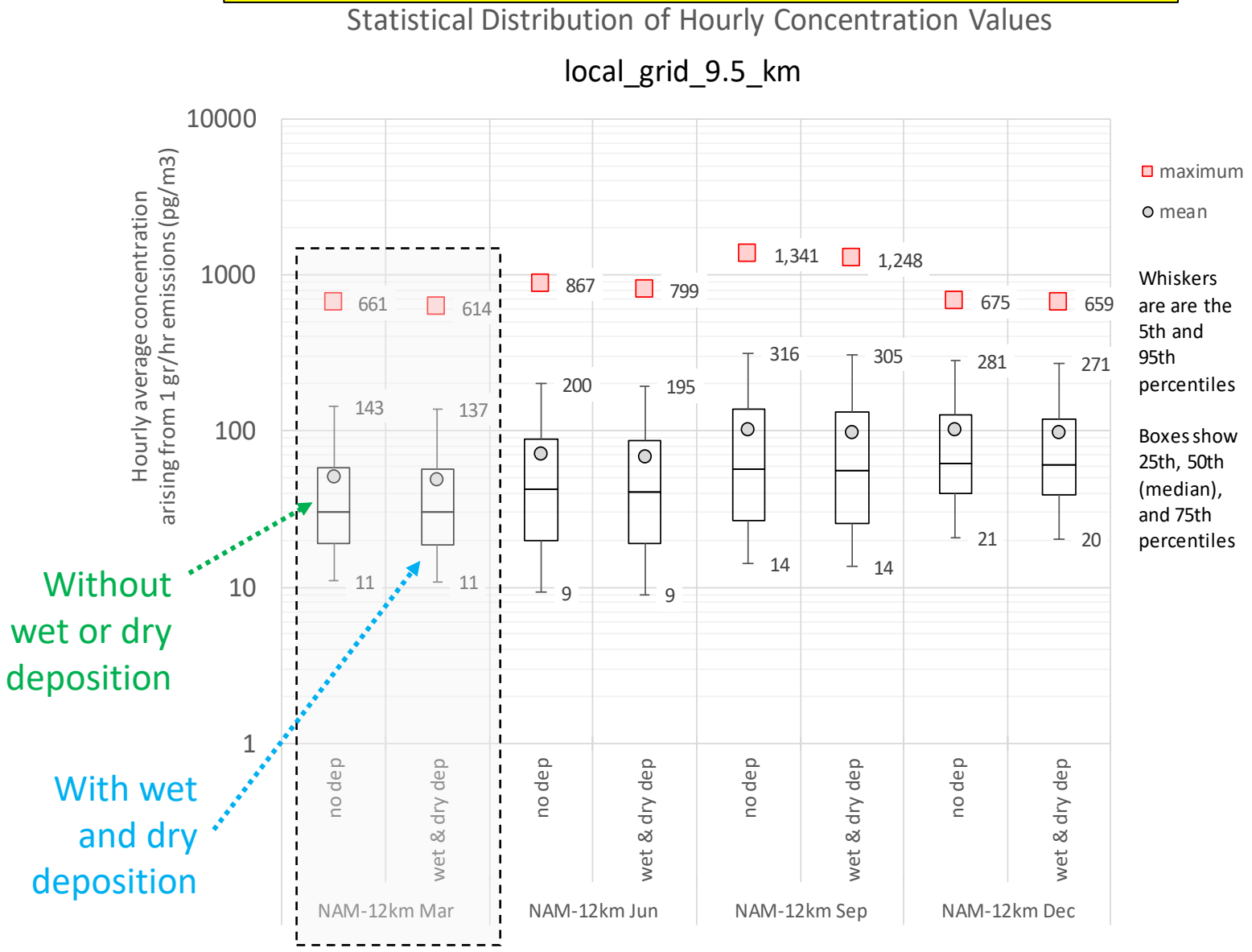
For maximum concentrations, little difference except for large particles (10 µm)

What physical-chemical properties could we conceivably use in HYSPLIT, if we had them?

- **Predicted phase in the atmosphere** *(e.g., vapor vs. particle)*
- **Dry Deposition Parameters**
  - if particle: *particle size, density, shape factor*
  - if vapor:
    - *surface reactivity factor*
    - *diffusivity ratio*
    - *effective Henry's Law Constant*
- **Wet Deposition Parameters**
  - if particle: *could probably use HYSPLIT defaults*
  - if vapor: *Henry's Law Constant*
- **Chemical Reactivity Parameters**
  - *e.g., half-life for reactions with OH•, O_3, etc.*

Examined all of these with comparable set of sensitivity simulations to see impacts on results…

Example of overall impact of wet/dry deposition (for SO_2)



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5. Recommendations

- PowerPoint
- Report
- EPI-Suite Outputs
- Spreadsheet with EPI and other data
- Scripts, Programs, etc.
- Model outputs
- Post-processing graphics

1. Physical-Chemical Properties
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5. **Recommendations**

Chemical-Physical Property or Parameter	Is experimental or theoretical estimate available for some or all compounds?	What is the impact of this factor on downwind concentrations?		Overall suggestion
Atmospheric Phase				
Vapor or Particle Phase	Vapor/particle partitioning estimates available for most compounds; most in the vapor phase	vapor-phase and particles less than 5 µm not dramatically different.		Unless other info available, assume all chemicals are in the gas-phase
Dry Deposition				
Particle size	Not generally available, but if conventional vapor/particle partitioning phenomena are involved, most particle-phase pollutant would be associated with relatively small particles, e.g., less than ~5 µm diameter.	The downwind concentrations particles less than 5 µm in diameter are not dramatically different. Larger particle sizes show significant depletions due to gravitational settling.		Most compounds can/should be treated as gas-phase, but if specific info suggests particle is in particulate phase, could assume ~5 µm diameter, if specific particle size info not available.
Specified Deposition Velocity	Not generally available, and of course depends on meteorological and surface conditions, but many pollutants have a deposition velocity (V_d) of 0.1 – 1 cm/sec under typical conditions.	**V_d (cm/sec)**	**reduction in downwind concentrations**	Could assume V_d=0 and create conservatively high estimate of downwind concentrations. If want to use this method, and without specific info, could assume 0.1 cm/sec, but this is somewhat arbitrary.
		<= 0.1	little impact	
		1	~50%	
		10	10-30x	
Surface Reactivity Factor	Varies from 0-1, but not generally available for most ALOHA compounds.	Very little impact on simulation results.		If using resistance method for dry deposition, could use a value of ~0.1 with little fear that results will be strongly influenced.
Diffusivity Ratio	Not generally available, but could be estimated with relatively well-established structure-property correlations, if desired.	Very little impact on simulation results.		If using resistance method for dry deposition, could use a value of ~2 with little fear that results will be strongly influenced.
Effective Henry's Law Constant	Henry's Law Constant (HLC) for most chemicals available, but effective value (HLC*) uncertain as it depends on the conditions, e.g., pH.	Very little impact on simulation results.		If using resistance method for dry deposition, could use standard HLC value, with little fear that results will be strongly influenced.

Chemical-Physical Property or Parameter	Is experimental or theoretical estimate available for some or all compounds?	What is the impact of this factor on downwind concentrations?	Overall suggestion
Wet Deposition			
Precipitation Rate	This is not a "chemical-specific" parameter, but the uncertainty introduced by using most meteorological data sets to drive the HYSPLIT model will generally be highly significant.	Moderate impacts on simulation results. In some cases, meteorological data set used for HYSPLIT will indicate significant precipitation, but there will be no actual precipitation. And vice versa.	Given uncertainty in model-precipitation, and danger of predicting artificially-low concentrations if modeled but not actual precipitation, recommend that wet deposition not be included in the typical simulation. If on-site observations, then perhaps this uncertainty can be reduced.
Henry's Law Constant	Henry's Law Constant (HLC) for most chemicals is available.	Moderate impact on results, when raining, and when HLC varied over large range.	If decide to include wet deposition, could use chemical-specific HLC
Below-Cloud Particle Scavenging Coefficient	This is primarily a physics parameter, and not a chemical-specific parameter. Could depend on particle size distribution and other factors that could be chemical-specific but which would largely be unknown.	Moderate impact on simulations results, when it is raining, and when WETC varied over large range, ***but it is unlikely that WETC will be that uncertain.***	If decide to include wet deposition, and if assuming chemical in particle phase, could use HYSPLIT default wet deposition parameters.
Chemical Transformations			
OH• Reaction	Estimates of reaction rate with OH• available for many compounds, but, need estimated OH• concentration, e.g., diurnal variation.	Most reactions rates low enough that impact will be minimal on downwind concentrations. But for a few compounds, impacts could be significant.	Recommend to not include. But, if desired, OH• estimate could be included in HYSPLIT, ported over from HYSPLIT-SV and HYSPLIT-Hg.
O_3 Reaction	Estimates of reaction rate with O_3 available for a some compounds, but, need estimated O_3 concentrations, e.g., diurnal variations.	Most reactions rates low enough that impact will be minimal on downwind concentrations. But for a few compounds, impacts could be significant.	Recommend not to include. But, could have rates for some chemicals, and some methodology for estimating O_3 concentration.
Other Transformations	Potentially there are other reactions and/or transformations that could be considered, e.g., photolysis, rxn with NO_3, etc., but would be a challenge to estimate rates and reactants.	Would be relatively small impact unless rate was "fast"	Recommend not to include, unless more information developed.

Possible Approaches:

1. No deposition or transformation – this may be the most sensible approach…

2. Vapor phase, dry deposition via resistance method, using HLC (not HLC*), and assumed values for Diffusivity Ratio and Surface Reactivity

3. Vapor phase, dry dep as above, + wet dep using HLC

4. Add in reaction with OH•, with or without deposition, and add a subroutine to HYSPLIT that estimates OH•

5. Additionally, add in reaction with O_3, with or without deposition, and add an O_3-estimation subroutine to HYSPLIT

6. Consider more complex physical-chemical processes…

Given the inherent uncertainty in model-estimated precipitation, and the danger of predicting artificially low air concentrations if there is modeled but not actual precipitation, *it is being recommended here that wet deposition not be included in the typical CAMEO-ALOHA HYSPLIT-based simulation.*

If on-site observers are able to estimate the precipitation rate, then perhaps this uncertainty can be reduced.

An argument can be made that deposition and transformation should not be included in emergency response simulations for any given chemical for one or more of the following reasons:

- Exclusion of deposition and transformation will provide a conservatively high estimate, without the danger of underestimating downwind concentrations if the deposition and/or transformation is overestimated.
- The simulation of the fate processes is relatively uncertain, due to limited information about the relevant parameters and/or limitations in the physics and chemistry of the simulation itself.
- In many cases, the specification of chemical-specific fate parameters will not have a dramatic impact on the simulation results, especially for local impacts.
- Meteorological factors such as wind speed and direction, and precipitation rate, are relatively uncertain and may exert a much more significant influence on downwind concentrations than any chemical-specific fate phenomena
- Other simulation parameters, particularly the emissions rate, will also generally be relatively uncertain and may exert a much more significant influence on downwind concentrations than any chemical-specific fate phenomena


Thanks